WEST

Generate Collection Print

L19: Entry 1 of 2 File: USPT May 19, 1998

DOCUMENT-IDENTIFIER: US 5753008 A
**** See image for Certificate of Correction ****
TITLE: Solvent resistant hollow fiber vapor permeation membranes and modules

Abstract Text (1):
A vapor permeation method and apparatus for removing a vapor from a vaporous feed stream, the method and apparatus utilizing highly solvent-resistant composite hollow fiber membranes and a permeate flow countercurrent to the feed flow, wherein the support of the composite membrane is formed by solution casting and has been rendered sufficiently solvent-resistant by a post-casting step to retain at least 20 of its burst pressure when soaked in the solvent used to cast the support.

Brief Summary Text (10):
It is a still further object of the present invention to provide a novel, highly selective composite hollow fiber membrane.

Brief Summary Text (13):
The present invention comprises a novel vapor permeation method and apparatus. The apparatus comprises a bundle of thin-film composite hollow fibers arranged substantially parallel to each other in a chamber or module with a means for removing permeate vapor located near the feed end of the module so as to cause the flow of permeate to be countercurrent to that of the flow of the feed. The composite fibers in the module comprise support fibers of very high permeability and solvent-resistance and a thin, permselective coating on the surface of the support fibers. The support fibers are formed from a polymer dissolved in a solvent and then rendered solvent-resistant in a post-treatment step. In two closely related aspects of the invention, a class of highly selective coatings for the composite fibers has been discovered, as well as an improved method of using the hollow fiber vapor permeation membranes that utilize a countercurrent condensable sweep gas.

Brief Summary Text (21):
(b) a bundle of thin film composite hollow fiber membranes arranged substantially parallel to each other in the chamber, each of the composite hollow fiber membranes comprising

Brief Summary Text (26):
(a) contacting a feed stream comprising a first vapor and at least one additional vapor with the feed side of thin film composite hollow fiber membranes arranged substantially parallel to each other in a chamber having feed and retentate ends, each of the composite hollow fiber membranes comprising

Brief Summary Text (40):
In addition, the permeability of the support fiber must be sufficiently high so that it does not provide a major resistance to the flow of permeate through the composite membrane. This high permeability must be retained even after the post-treatment step. Generally, the permeability of the fibers to dry nitrogen should be greater than 5 normal cubic meters per square meter per hour per atmosphere driving force (Nm.sup.3 /m.sup.2 .multidot.hr.multidot.atm), and more preferably greater than 50 Nm.sup.3 /m.sup.2 .multidot.hr.multidot.atm.

Brief Summary Text (44):
For the removal of water vapor from other vapors, it is best that the permselective

coating material be more permeable to water vapor than to other components in the feed stream. In this case, the material is preferably very hydrophilic. Examples of perm-selective coating materials useful for removing water from organics include polyvinyl alcohol, cellulosic materials, chitin and derivatives thereof, polyurethanes, polyamides, polyamines, poly(acrylic acids), poly(acrylates), poly(vinyl acetates), and polyethers. Other polymers normally viewed as not especially hydrophilic (e.g., polyolefins, polystyrene, and poly-acrylates) can be rendered sufficiently hydrophilic to be useful as membrane materials by incorporating hydrophilic groups such as hydroxyl, amine, carboxyl, ether, sulfonate, phosphonate, quaternary amine, and ester functionalities. Such groups can be incorporated by choosing monomers that contain such groups or by adding them in a post-treatment step such as radiation- or plasma-grafting. Blends and copolymer versions of these materials are also useful. The coating material should also be cross-linked to provide sufficient resistance to swelling or dissolution by components of the feed stream.

Brief Summary Text (46):
For the removal of volatile compounds from water vapor, the permselective coating is usually, but not always, an elastomeric or rubbery polymer. Examples of materials useful for such separations include natural rubber; nitrile rubber; polystyrene-butadiene copolymers; poly(butadiene-acrylonitrile) rubber; polyurethanes; polyamides; polyacetylenes; poly(trimethylsilylpropyne); fluoroelastomers; poly(vinylchlorides); poly(phosphazenes), particularly those with organic substituents; halogenated polymers, such as poly(vinylidene fluoride) and poly(tetrafluoroethylene); and polysiloxanes, including silicone rubber. Blends and copolymer versions of these materials are also useful. Ion-exchange membranes and composites may also be used for some applications. A particularly preferred coating for the removal of volatile compounds from water vapor is poly(dimethyl-siloxane) and derivatives thereof.

Detailed Description Text (3):
To a 2-liter resin kettle equipped with an overhead stirrer and a nitrogen sparge was added 1033 g of NMP and 108.1 g of oxydianaline (ODA). Next, 2.0 g of phthalic anhydride (an end-capping agent) was added. Then, 104.8 g of benzophenone tetracarboxylic acid dianhydride (BTDA) and 47.0 g of pyromellitic dianhydride (PMDA) were added in three portions over a 3-hour period. The mixture was then stirred overnight. This resulted in the formation of a BTDA/PMDA/ODA copolyamic acid solution containing 20 wt % solids. The molar ratio of BTDA/ODA to PMDA/ODA was 1.5. The Brookfield viscosity of the copolyamic acid solution at 30.degree. C. was 35,000 cp.

Detailed Description Text (11):
Preparation of Solution C: 10 g of succinic anhydride and 5 g of 1M HCl were dissolved in 85 g of hot (65.degree. C.) EtOH, and then allowed to cool.

Detailed Description Text (13):
Application of the Coating: The lumens of the hollow fibers of Example 1 were filled with the coating solution for 1 minute, and then drained by the force of gravity. Dry nitrogen at room temperature was first forced through the lumens of the fibers for 10 minutes; then repeated for another 10 minutes. Hot nitrogen at 80.degree. C. was then forced through the lumens of the fibers for 2 hours. The temperature of the nitrogen was then increased to 130.degree. C. and the procedure repeated for 3 hours. Finally, dry nitrogen at ambient temperature was forced through the lumens of the fibers overnight. The resulting composite hollow fibers had a permeability to dry nitrogen of between 0.001 and 0.002 Nm.sup.3 /m.sup.2 .multidot.hr.multidot.atm at a pressure of 7.8 atm.

Detailed Description Text (15):
A bundle of 20 hollow support fibers made by the method of Example 1 except with an internal diameter of 280 .mu.m, were incorporated into a module using an epoxy potting compound. The module was equipped with a permeate port located near its feed end. The effective length and area of the fibers were 38 cm and 67 cm.sup.2, respectively. A permselective coating was formed on the inside surfaces of the fibers in this module using the procedure described in Example 2, thus forming a composite hollow fiber vapor permeation module.

Detailed Description Text (18):
A composite hollow fiber module essentially the same as that described in Example 3 except that the module contained 30 fibers with inside diameters of 330 .mu.m and having 118 cm.sup.2 of surface area was operated in a vapor permeation test on a feed solution of 10.2 wt % water in MeOH at 72.degree. C. The permeate pressure was maintained at 0.02 atm. The results of this test are given in Table II.

Detailed Description Text (20):
A composite hollow fiber module essentially the same as that described in Example 3 except that the module contained 50 fibers with inside diameters of 320 .mu.m and having 191 cm.sup.2 of surface area was operated in a vapor permeation test on a feed solution of 4.9 wt % water in EtOH at 93.degree. C. The permeate pressure was maintained at 0.01 atm. The results of this test are given in Table II.

Detailed Description Text (22):
A composite hollow fiber module of essentially the same as that described in Example 3 was made except that the module contained 38 fibers with inside diameters of 365 .mu.m and having 166 cm.sup.2 of surface area and inside surfaces were coated with a cross-linked PVA. This module was operated in a vapor permeation test on a feed mixture of 16 wt % water in MeOH at 77.degree. C. and a feed pressure of 1.1 atm. The permeate pressure was maintained at 0.1 atm. In addition, a condensable sweep stream comprising 100% MeOH at 75.degree. C. and 0.1 atm was introduced to the permeate side of the membrane at a sweep inlet port located near the retentate end of the module so as to flow countercurrent to the flow of the feed.

Detailed Description Text (26):
A composite hollow fiber module of essentially the same design as that described in Example 3 was made except that the module contained 38 fibers with inside diameters of 360 .mu.m and having 166 cm.sup.2 of surface area. A permselective coating of cross-linked polydimethyl-siloxane (PDMS) was placed on the inside surfaces of the fibers using the following procedure. The lumens of the hollow fibers were filled with a solution of 10 wt % PDMS (Sylgard 184 from Dow) in toluene for 1 minute. The lumens were then drained and dry nitrogen was forced through the lumens for 10 minutes; then repeated for another 10 minutes. Hot air at 100.degree. C. was then forced through the lumens for 2 hours. Ambient temperature air was then blown through the fiber lumens overnight. The resulting composite hollow fiber module had a permeability to dry nitrogen of 0.05 Nm.sup.3 /m.sup.2 .multidot.hr.multidot.atm and a selectivity for oxygen over nitrogen of 2.1 when tested on pure gases at 8 atm.

Current US Cross Reference Classification (4):
210/640

CLAIMS:

1. A vapor permeation module for removing a first vapor from a feed stream comprising a mixture of vapors not containing any liquid, the module comprising:

(a) a chamber having feed and retentate ends and means for removing permeate vapor near the feed end;

(b) a bundle of thin film composite hollow fiber membranes arranged substantially parallel to each other in said chamber, each of said composite hollow-fiber membranes comprising:

(i) a highly permeable solvent-resistant hollow support fiber comprising a polymer selected from the group consisting of polyimides, polybenzimidazoles, polyphenylquinoxolanes, and polymers with pendant or terminal cross-linkable groups, said support fiber having been formed from a polymer dissolved in a solvent and then rendered solvent-resistant in a post-treatment step, wherein said solvent-resistant hollow support fiber retains at least 20% of its burst pressure when soaked in said solvent used to form said polymer solution, and

(ii) a permselective coating on the surface of said support fiber, said

permselective coating being a cross-linked polymer selected from the group consisting of poly (acrylic acids), poly (acrylates), polyacetylenes, poly (vinyl acetates), polyacrylonitriles, polyamines, polyamides, polyethers, polyurethanes, polyvinyl alcohols, polyesters, cellulose, cellulose esters, cellulose ethers, chitosan, chitin, polymers containing hydrophilic groups, elastomeric polymers, halogenated polymers, fluoroelastomers, polyvinyl halides, polyphosphazenes, poly (trimethylsilylpropyne), polysiloxanes, poly (dimethyl siloxanes) and copolymers and blends thereof, and having a selectivity of at least 5 for said first vapor over at least one other vapor in said mixture of vapors; and

(c) means for securing and sealing said bundle of hollow fiber membranes to said chamber at said feed and retentate ends so as to permit fluid communication with said feed gas.

2. The module of claim 1 wherein said feed stream is directed to the inside of said composite hollow fiber membranes.

3. The module of claim 1 wherein said feed stream is directed to the outside of said composite hollow fiber membranes.

32. A vapor permeation process comprising:

(a) contacting a vaporous feed stream containing a first vapor and at least one additional vapor with the feed side of thin film composite hollow fiber membranes arranged substantially parallel to each other in a chamber having a feed end and a retentate end, each of said composite hollow fiber membranes comprising:

(i) a highly permeable solvent-resistant hollow support fiber comprising a polymer selected from the group consisting of polyimides, polybenzimidazoles, polyphenylquinoxolanes, and polymers with pendant or terminal cross-linkable groups, said support fiber having been formed from a polymer dissolved in a solvent and then rendered solvent-resistant in a post-treatment step whereby said solvent-resistant hollow support fiber retains at least 20% of its burst pressure when soaked in said solvent used to form said polymer solution, said post-treatment step being selected from heat treatment and exposure to radiation selected from the group consisting of UV, microwave, and X-ray radiation, and electron beams, and

(ii) a permselective coating on the surface of said support fiber, said permselective coating being a cross-linked polymer selected from the group consisting of poly (acrylic acids), poly (acrylates), polyacetylenes, poly (vinyl acetates), polyacrylonitriles, polyamines, polyamides, polyethers, polyurethanes, polyvinyl alcohols, polyesters, cellulose, cellulose esters, cellulose ethers, chitosan, chitin, polymers containing hydrophilic groups, elastomeric polymers, halogenated polymers fluoroelastomers, polyvinyl halides, polyphosphazenes, poly (trimethylsilylpropyne), polysiloxanes, poly (dimethyl siloxanes) and copolymers and blends thereof, and having a selectivity of at least 5 for said first vapor over at least one other vapor in said mixture of vapors;

(b) permitting said first vapor in said feed stream to permeate from the feed side to the permeate side of said hollow fiber membranes to form a permeate stream enriched in said first vapor and a retentate stream depleted in said first vapor; and

(c) removing said permeated stream enriched in said first vapor from said chamber near the feed end of said chamber.

33. The process of claim 32 wherein said feed stream is directed to the inside of said composite hollow fiber membranes.

44. The process of claim 32 wherein said feed stream is directed to the outside of said composite hollow fiber membranes.

55. The process of claim 54 wherein said hydrophilic permselective coating is selected from the group consisting of polyamides, polyvinylalcohols, polyesters, cellulose, cellulose esters, cellulose ethers, polyurethanes, chitosan, chitin,

polyacrylonitriles, polyamines, polyacetylenes, and copolymers and blends thereof.

57. A vapor permeation process comprising:

(a) contacting a vaporous feed stream containing a first vapor and at least one additional vapor with the feed side of thin film composite hollow fiber membranes arranged substantially parallel to each other in a chamber having feed and retentate ends, means for introducing a sweep stream at the retentate end of said chamber and means for removing permeate at the feed end of said chamber, each of said composite hollow fiber membranes comprising:

(i) a highly permeable solvent-resistant hollow support fiber, comprising a polymer selected from the group consisting of polyimides, polybenzimidazoles, polyphenylquinoxolanes, and polymers with pendant or terminal cross-linkable groups, said support fiber having been formed from a polymer dissolved in a solvent and then rendered solvent-resistant in a post-treatment step, whereby said solvent-resistant hollow support fiber retains at least 20% of its burst pressure when soaked in said solvent used to form said polymer solution, said post-treatment step being selected from heat treatment and exposure to radiation selected from the group consisting of UV, microwave, and X-ray radiation, and electron beams, and

(ii) a permselective coating on the surface of said support fiber, said permselective coating being a cross-linked polymer selected from the group consisting of poly (acrylic acids), poly (acrylates), polyacetylenes, poly (vinyl acetates), polyacrylonitriles, polyamines, polyamides, polyethers, polyurethanes, polyvinyl alcohols, polyesters, cellulose, cellulose esters, cellulose ethers, chitosan, chitin, polymers containing hydrophilic groups, elastomeric polymers, halogenated polymers, fluoroelastomers, polyvinyl halides, polyphosphazenes, poly (trimethylsilylpropyne), polysiloxanes, poly (dimethyl siloxanes) and copolymers and blends thereof, and having a selectivity of at least 5 for said first vapor over at least one other vapor in said mixture of vapors; and

(b) directing a sweep stream to the permeate side of said hollow fiber membranes by said means for introducing a sweep stream in a manner such that the flow of said sweep stream is substantially countercurrent to the flow of said feed stream, thereby transporting at least a portion of said first vapor from said feed side to said permeate side of said membrane to form a combined permeate side mixture of said sweep stream and said first vapor;

(c) removing a retentate stream from said retentate end of said chamber that is depleted in said first vapor; and

(d) removing said combined permeate side mixture from said means for removing permeate.